

LABORATORY INVESTIGATION OF VISIBLE SHUTTLE GLOW MECHANISMS

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ABSTRACT

Laboratory experiments designed to uncover mechanistic information about the spectral and spatial characteristics of shuttle glow were conducted. The luminescence was created when a pulse of O atoms traveling at orbital velocities was directed toward NO molecules previously adsorbed to aluminum, nickel, and Z306 Chemglaze (a common baffle black) coated surfaces held at various temperatures.

Spectral and spatial measurements were made using a CCD imaging spectrometer. This instrument is identical to the one used in flight studies except for the substitution of a CCD array rather than photographic film at the focal plane. Corroborative spectral information was recorded in separate measurements using a scanning monochromator and gated photomultiplier arrangement. The surface mediated laboratory luminescence was found to be spectrally similar to space borne observations of the visible shuttle glow phenomena and to the red of the gas phase recombination previously reported at thermal energies and observed at orbital energies in the present work. Relative intensities above the three materials studied were found to be within a factor of two at liquid nitrogen temperatures. Spectral observations above the aluminum and chemglaze samples were similar but nickel was consistently shifted further to the red by approximately 30 nanometers. The intensity above a given surface was found to vary inversely with temperature increasing an order of magnitude as the temperature was dropped from ambient to liquid nitrogen (presumably due to enhanced NO accommodation).

The e-folding distance at several temperatures was calculated from images of the surface glow using the Photometrics image processing capability of the imaging spectrometer. The e-folding distance was not altered as a function of incoming O beam velocity (over the range 6-10 km/s tested). Plots of the projected e-fold distance versus the square root of temperature were linear implying a thermalization of the exiting species. These results coupled with the apparent need to utilize chemical energy in the removal of product species bound to the surface (as evidenced by the spectral shift observed in the heterogeneous recombination spectra as a function of distance from the interaction plate and concomitant increase in lifetime) led to an assumption of Maxwellian exit speeds. The consequence of such spatial measurements at 93 K leads to a computed average excited state lifetime on the order of 180 μ seconds. These observations provide direct evidence that the visible Shuttle glow results from recombination of oxygen atoms and surface bound NO.

Introduction

The visible glow above shuttle surfaces subjected to impact by energetic atmospheric species was first observed during the STS-3 Mission (Banks et al., 1983). Starting with the next mission Mende and coworkers undertook a series of systematic photographic observations which characterized the glow phenomenon (Mende et al., 1983a, b, 1984a, b, 1985, 1986, 1988; Swenson et al, 1985). The glow was present only above surfaces subjected to the direct impact of the residual atmosphere, suggesting that kinetic energy played a role (Mende et al., 1988, Slanger, 1987). Spectrally resolved observations revealed the glow as a broad band emission peaking at 680 nm. Because of the similarity of the spectrum to that of the NO₂ gas phase recombination, heterogeneous recombination mechanisms involving atomic oxygen and NO at shuttle surfaces were postulated as the source of the glow (Swenson et al., 1985; Kofsky and Barrett, 1986). The glow brightness was inferred to vary inversely with temperature based on modeling of orbiter surface temperatures and NO surface

residence times (Swenson et al., 1986).

Recently two laboratory studies (Arnold and Coleman, 1988, Orient et al., 1990) of the surface mediated recombination of NO_2 using high velocity CW atomic oxygen beams have attempted to simulate the observed glow. Comparisons between their observations and results obtained in the present pulsed study reveal mechanistic features of the proposed luminescence processes.

Space borne measurements also revealed a characteristic spatial extent of the observed luminescence. The glow thickness is a result of the convolution of excited state lifetimes and the distribution of exit velocities of the emitting species from the interaction surface. Since the exact nature of the NO_2 formation mechanism is still debated, questions of recoil energy, thermalization, and excited state lifetime are still open to speculation. To further complicate matters the excited state lifetimes reported in the literature range from $1\mu\text{s}$ measured by Sackett and Yardley (1971) to $170\text{--}260\mu\text{s}$ reported by Donnelly and Kaufman (1977). Variations between the lifetimes of NO_2 have been attributed to mixing of the $^2\text{B}_1$ and $^2\text{B}_2$ states or explained in terms of one or more of these excited state variably coupled to the high vibrational levels of the $^2\text{A}_1$ ground state (Douglas 1966, Paulsen 1970, Alder- Golden 1989) yielding a wide range of values. Considerable variation in lifetimes based solely upon emission criterion have also been reported. The common assumption of a $70\mu\text{sec}$. lifetime quoted in the analysis of flight data forces an emitter velocity greater than the spacecraft surface temperature would provide and hence has generated a discussion of the possible transfer of ram energy.

An Ely-Rideal recombination process in which an incoming O atom pulls off a surface bound NO to form the excited state species might transfer some of the ram kinetic energy to the NO_2 product in an amount reduced by small losses to the surface. However, ejection of an excited NO_2 molecule with thermalized kinetic energy is expected if NO_2 is formed via the Langmuir-Hinselwood surface migration processes.

This report describes direct laboratory tests of these mechanistic tenants. Good agreement with spectra observed in orbit both in terms of spectral distribution and observed temperature scaling were observed. In addition, the results of this study suggest that thermalization even at high O atom velocities common to the ram interactions of the shuttle is likely, but cannot rule out a Rideal interaction hypothesis.

Experimental

Atomic oxygen with a velocity of 8 km/s was produced in a large vacuum chamber via a pulsed laser discharge technique (Krech and Caledonia, 1986) and was directed onto targets located 85 cm down stream from the O-atom source. The apparatus has been described in greater detail previously (Caledonia, 1989; Holtzclaw et al., 1990). Six by six inch targets of aluminum, nickel and Z306 Chem-glaze paint were mounted on a reservoir which could be filled with liquid nitrogen. Target temperature was monitored with a copper-constantan thermocouple probe calibrated by immersion into water/ice, dry ice/ethanol, and liquid nitrogen baths.

The surfaces were selectively doped prior to oxygen exposure with a purified pulse of NO. Residual non adsorbed gas was removed from the chamber during a pump out interval prior to O atom interaction. NO (stated purity >98.5 percent) was first passed through an Ascarite column to remove residual NO_2 prior to sample dosing. Dosing was performed with a small solenoid valve (General Valve series 9) placed directly in front of the target. NO flow was monitored with a mass flow meter and was typically 0.007 standard cc's per pulse. A pulse of NO was delivered to the target prior to every O-atom pulse. The NO mass flow rate was specified such that less than one monolayer of NO impinged the target with each pulse. The relatively high vapor pressure of NO, even at 77 K , precluded the buildup of a thick NO film on the target surfaces. A sufficient delay ($\sim 1\text{s}$) between the NO and O-atom pulses was used to insure that all NO was evacuated from the chamber before the next oxygen atom pulse ($p < 10^{-5}$ torr). This precaution is important since gas phase reactions of O and NO could produce interfering emissions (Fontijn, 1964). Typical fast O-atom fluence levels for these tests were $1 \times 10^{14}\text{ cm}^{-2}$ per pulse.

Spectral and spatial information was taken using a CCD imaging spectrometer designed at Lockheed that has been used to photographically record the glow observed above the space shuttle in low Earth orbit. The instrument as employed in these experiments is identical to that used for the orbital studies (Swenson et al., 1985) except that an unintensified 378×576 -line CCD array in a Photometrics model 3000 camera was substituted for the photographic film. The instrument has provision for removing the slit and grating from the optical axis wherein the instrument is an imager.

Spatial image measurements were performed upon surfaces at room temperature and when cooled to liquid nitrogen temperature. In addition, images were gathered of the interaction plume as a function of O atom velocity from 5km/s-10km/s. The inside of the chamber was blackened to minimize reflections which might obstruct the image. The instrument processor permitted real time display, background subtraction, and image analysis during these experiments.

With the the slit and grating inserted into the optical path, the instrument is a spectrometer with y axis wavelength dispersion (spectral resolution ~ 7 nm) as a function of the x (distance) axis of the array. Confirming spectral information was recorded in separate measurements using a scanning monochromator and photomultiplier tube where the signal processing was performed with a gated photon counter. The spectral resolution of the monochromator was 2.7 nm. The relative spectral response of the CCD imaging spectrometer was determined using an NBS referenced quartz halogen lamp. Wavelength position and spectral resolution were determined using Hg and Ne line sources. The spectral response of the monochromator was determined by viewing the gas phase reaction of O and NO in a flow tube. This reaction has long been used as a secondary standard for spectral calibrations in the visible region of the spectrum (Fontijn, 1964).

Spectral Results :

An image of the surface glow above an NO-doped Z306 Chem-glaze coated foil held at ~ 93 K taken with the imaging spectrometer is shown in Figure 1. The oxygen atom beam enters from the left and envelops the whole of the target. A separate nozzle also to the left is used to inject NO on the surface. This image was integrated over ~ 100 pulses of the beam. The black strip in the center of the image demarks the slit position. As mentioned above, when the slit and grating are inserted into the optical path, the instrument is a spectrometer with wavelength dispersion along the y axis of the array as a function of x distance from the target plate as shown in the inset of the figure.

The spectral distribution of the glow observed under these conditions was measured in separate tests using either the scanning monochromator or the CCD array-spectrometer. These observations are contrasted in Figure 2 with spectra measured from the Space Shuttle.

All spectra have been smoothed for ease of comparison. The shuttle data (Mende et al., 1988) was taken with an imaging spectrometer similar to that used in the laboratory, but using film rather than a CCD array (Swenson et al., 1985). Intensities were obtained from densitometry traces and corrected for window transmission and film response. The laboratory spectra are in reasonable agreement with the observed Shuttle glow. The monochromator data displays a similar onset and the imaging spectrometer exhibits a similar spectral shape. Spectra obtained with the imaging spectrometer were found to fall symmetrically within the respective spectral envelope measured with the monochromator with similar wavelength maxima. The variation between the scanning monochromator and the imaging spectrometer spectra could be the result of calibration uncertainties; as described in the previous section the calibration procedures employed for the two diagnostics were quite distinct. The differences observed between laboratory and Shuttle glows may be within the cumulative experimental uncertainties in both the laboratory and flight data correction procedures. All three spectra suspected to result from surface mediation are significantly shifted from the gas phase three body NO_2 recombination spectra also shown in Figure 2. The magnitude of the observed shifts are in line with typical surface physisorption energies. In fact, the spectral shift of ~ 80 nm between the gas/gas and surface mediated spectra obtained in this work is thought to be the result of surface bond energy expended in the removal of NO_2^* from the target.

Measurements were performed in the absence of a target to examine the luminescence resulting from the NO gas phase collisions with the O beam employed in the present study. The gas phase luminescence is blue shifted relative to the surface glow described above, peaking at ~ 625 nm as in thermal recombination. Note that the mechanism producing the gas phase luminescence observed in this work has not been identified. NO recombination with collisionally slowed oxygen atoms or fast atom interactions with NO dimers may occur. The NO-NO dimer bond energy is only on the order of 0.06 eV.

Since the targets were limited to approximately monolayer coverage of NO, any material dependence observed will reflect differences in material adsorption properties relating to the heterogeneous recombination process. Luminescence measurements were performed on NO-doped

cooled targets of Z306, nickel and aluminum. In all cases the observed intensities were similar in magnitude (factor of two, we did not evaluate the variability in adsorbed NO amongst these materials). The spectral distributions for the three materials are quite similar with the exception that the spectra on nickel appears red-shifted by approximately 30 nanometers. The delineation of any material dependencies will require careful acquisition of a larger database than provided to date.

A similar set of measurements were made for room temperature targets of Z306 and aluminum. All other experimental conditions were held the same. For these cases the surface glow was spectrally similar to that observed on the cooled samples but the intensity levels were down by an order of magnitude. This inverse temperature dependence may reflect the fact that more NO can be accommodated on surfaces as they are cooled. Swenson et al. (1986) have analyzed Shuttle glow data from various missions and show that the glow intensity drops approximately an order of magnitude as the surface temperature is decreased from room temperature to 173 K. Laboratory measurements at additional temperatures would elucidate the exact nature of this correlation of intensity as a function of temperature.

Spatial Results :

Images of the luminescent plumes created by the interaction of a pulse of O atoms with previously NO doped surfaces were recorded utilizing the CCD imaging spectrometer. A background subtraction provided difference images. Exposures integrating 100 such pulsed events were taken using a 35 mm lens at various surface temperatures. The overplot on the 93 K image shown in Figure 1 displays the intensity drop off of the glow from the surface using the Photometrics image processing capability. The plot shows the relative intensity of a set of row elements selected from the image matrix array versus pixel location. As mentioned above, the black rows in the center of the image correspond to the position of the interchangeable slit which was removed during image measurements. An image of the NO nozzle provided a reticle to benchmark the spatial length represented by each pixel number. A narrow band of rows were selected symmetric about this vacant slit position for analysis. A uniform field correction on the order of 10 percent at the periphery was made by imaging a large uniformly illuminated diffuse plate.

Figure 3 shows a corrected intensity plot as a function of position in centimeters from the surface (derived from the image shown earlier in Figure 1) which is approximately linear when plotted on a logarithmic scale (see inset). Similar plots of pairs of such central row regions for a given image taken symmetrically about the slit region were found to be virtually identical.

Image data taken as a function of temperature and incoming O beam velocity were similarly analyzed. A few images were clearly obstructed by scattering but most displayed an exponential decay in intensity with distance from the interaction surface. The e-folding distance (distance over which the intensity drops to $1/e$ of the initial value) was calculated for each experimental condition. This parameter is of interest since the number of molecules in the excited state decays exponentially as $\exp(-t/\tau)$. Multiplying the top and bottom of this exponent by the mean molecular speed characteristic of the product exit velocity distribution yields the expression $\exp(-d/v\tau)$. Hence the e-fold (e^{-1}) distance d can be equated to the molecular velocity v times the average lifetime τ of the excited molecules.

No change in this e-folding distance (measured at 93 K) was observed as a function of initial O beam energy over the velocity range from 6 to 10 km/s tested. Thus increasing the translational energy of the incoming species within this range does not seem to impart any additional exit energy to the products formed by surface interaction. However, this result alone does not distinguish between a Langmuir-Hinshelwood or Rideal mechanism.

The calculated e-folding distances as a function of the square root of the plate temperature (in K) are plotted in Figure 3. The e-folding distance increases in rough proportion to a square root dependence of the surface temperature. A linear fit is provided for comparison. Such behavior indicates that the interactions at the surface are thermalized and products are most likely ejected with root mean squared exit velocities determined by the surface temperature in a Maxwellian fashion i.e. $v = \sqrt{3RT/M}$.

The low number densities of interacting species suggest a collisionless analysis regime with long mean free path. If the species are thermalized as they react at the surface and no elastic energy or momentum is imparted to the exiting products, then the assumption of a Lambertian directional distribution of these exiting species with Maxwellian speeds

can be invoked. Under such an assumption no influence due to incoming beam profile is expected since no translational energy is transferred. As seen in Figure 1, the glow thickness is not uniform but diminishes at the edges since the interaction plate is of finite (6 inches in length) dimension. A flattened maximum spatial extent region above and below the slit position was found in each plume image distant enough from the edge to receive symmetrical contributions of the exiting species. A narrow set of rows within this region were selected to plot the intensity drop off as a function of position described above. The e-fold lengths described above are then projections along the line of sight of the distance these product molecular emitter species travel during their excited state lifetime. The average distance an emitter species travels in contributing to a line of sight pixel can be found by dividing the projected distance by the cosine of the half angle of 30° which demarks the solid angle into which half of these contributors are dispersed in accordance with a Lambert cosine distribution. The average molecular distance associated with the e-fold parameter at 93 K was determined to be 4.2 centimeters. A value between the root mean squared speed of 225 m/s or the most probable speed of 183 m/s indicative of the Maxwell distribution curve at 93 K can serve as an estimate of the exit speed. The lifetime of the excited state can be determined as the ratio of this characteristic glow thickness parameter divided by the assumed exit velocity. A lifetime of the excited species on the order of 185-225 μsec results from such a calculation.

Spectra as a function of position from the plate are obtained by selecting column elements from the inset array shown in Figure 1 at various x distances from the plate. A spectral red shift on the order of 30 nm. is observed in spectra 1.3 cm. removed from the plate as compared to that observed on the surface. A progressive red shifting is observed for spectral slices as a function of distance from the plate. Species with longer lifetimes are responsible for the spectral emission at incremental distances from the interaction surface. These observations are consistent with the loss of energy required for these relatively longer lived species to overcome physisorption bonds to remove these product species from the surface. Surface bound emitters not having expended such energy are relatively shorter lived and their higher energy emission is peaked to the blue. The lifetimes of NO_2^* have been shown to depend upon excitation

energy (Donnelly and Kaufman, 1978; Alder-Golden, 1989). The higher energy excitation is associated with a shorter lived species and vice versa.

Discussion

The laboratory glow data are in quite reasonable spectral agreement with Shuttle glow observations and also exhibit a similar inverse temperature dependence. These observations provide strong evidence that the Shuttle glow results from recombination of oxygen atoms and surface bound NO. The NO_2^* recombination spectra created by a laboratory pulse of atomic oxygen traveling at orbital velocities was shown to be red-shifted from the gas phase interaction because of surface mediation. Only small variations in spectra and intensity were observed from material to material.

As mentioned above, two recent laboratory studies (Arnold and Coleman, 1988, Orient et. al., 1990) of the surface mediated recombination of NO_2 using high velocity CW atomic oxygen beams have attempted to simulate the observed glow. The first of these (Arnold and Coleman, 1988) directed a supersonic (1.4 km/s) beam containing oxygen atoms and an effusive NO beam at a nickel surface. The observed luminescence was observed to peak at 830 nm, well to the red of both the flight measurements of Shuttle glow and spectra obtained in the present pulsed study on nickel surfaces. A velocity effect may be indicated by this comparison, although such a dramatic shift to the red may also be related to the alternate removal of a more tightly bound surface O atom by NO. In addition, the presence of excited oxygen molecules can also produce an NO_2 spectra to the red of that created by $\text{O} + \text{NO}$ (Kenner and Ogryzlo 1984). More recently, (Orient et. al. 1990) directed an 8 km/s O beam and a jet of NO onto a MgF_2 surface. Their observations include a broad visible emission spectra peaked at 625nm which is similar to that observed in the present study when the gas pulses were allowed to interact prior to dopant isolation in the presence of a surface. Their light collection technique is not capable of spatial differentiation of the glows created as done in the present study.

It should be noted that the fast atom source used in these studies is not composed entirely of ground state oxygen atoms. Oxygen molecules are present at a concentration <20 percent and the metastable $\text{O}(1D)$ density in the beam has not been measured. Although the concentration of this latter species is estimated to be low, based upon quenching rate

constants for O(1D) by O and O₂ (Davidson et al, 1976) its potential contribution to the observed luminescence cannot be ascertained. This species is of course also present in the ambient atmosphere and its reactivity should be investigated independently.

Recently, a discussion of lifetimes and recoil energies involved in reconciling the flight data for various mechanisms proposed was provided by Slanger. Slanger suggests that translational energies in the 0.3 -1 eV range with radiative lifetimes between 100-200 μ s are most compatible with existing evidence. Our measurements appear to be consistent with these predictions. No difference in e-fold was found by varying the impinging O atom velocity but a direct measure of product exit velocities was not undertaken. The possibility of a momentum exchange contribution which does not vary with the velocity of the incoming species is possible, but the energy lost to the surface which manifests itself as a spectral shift must be considered. The red shift in the NO₂ spectrum has been thought to indicate that internal chemical energy is needed to break the surface bond and that O atom collisional energy is not efficient in removing the product species from the surface. A red shift similar to the flight results was observed in these heterogeneous O + NO laboratory experiments.

It should be noted that exit velocities for erosion glows (Holtzclaw et.al. 1990) using a similar beam source were measured to be 1.3 km/s. Erosion glow processes result from quite different mechanisms in which a material's chemical bond is broken. If exit velocities of this magnitude (1 Km/s) are shown to be involved, the above mentioned calculated lifetimes would be reduced on the order of less than 35 μ seconds. The present results argue against other than thermalized velocities and direct time of flight measurements of the product exit velocities in these surface mediated O + NO recombination studies are planned.

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REFERENCES

- Alder-Golden, S.M., The $\text{NO} + \text{O}$ and $\text{NO} + \text{O}_3$ Reactions, *J. Chem. Phys.*, **9** 3, 684-697 1989.
- Arnold, G.S. and Coleman, D.J., Surface Mediated Radical Recombination Luminescence: $\text{O} + \text{NO} + \text{Ni}$, *J. Chem. Phys.* **8** 8, 7147, 1988.
- Banks, P.M., Williamson, P.R., and Raitt, W.J., Space Shuttle Glow Observations, *Geophys. Res. Lett.* **1** 0, 118, 1983.
- Caledonia, G.E., Krech, R.H., and Green, B.D., A High Flux Source of Energetic Atoms for Material Degradation Studies, *AIAA J.* **2** 5, 59, 1987.
- Caledonia, G.E., Laboratory Simulations of Energetic Atom Interactions Occurring in Low Earth Orbit, in *Rarefied Gas Dynamics: Space Related Studies*, Vol. 116 of *Progress in Astronautics and Aeronautics*, AIAA, Washington, DC, pp. 129-142, 1989.
- Davidson, J.A., Sadowski, C.M., Schiff, H.I., Streit, G.E., Howard, C.J., Jennings, D.A., and Schmeltekopf, A.L., Absolute Rate Constant Determinations for the Deactivation of $\text{O}(1\text{D})$ by Time Resolved Decay $\text{O}(1\text{D}) \rightarrow \text{O}(3\text{P})$ Emission, *J. Chem. Phys.* **6** 4, 57, 1976.
- Donnelly V.M., Kaufman F., Fluorescence lifetime studies of NO_2 I. Excitation of the perturbed ${}^2\text{B}_2$ state near 600nm. *J. Chem. Phys.* **6** 6, 4100-4110, 1977.
- Donnelly V.M., Kaufman F., Fluorescence lifetime studies of NO_2 II. Dependence of the perturbed ${}^2\text{B}_2$ state on excitation energy. *J. Chem. Phys.* **6** 9, 1456-1460, 1978.
- Douglas, A.E., Anomalous Long Radiative Lifetimes of Molecular Excited States *J. Chem. Phys.* **4** 5, 1007, 1966.
- Fontijn, A., Meyer, C.B., and Schiff, H.I., Absolute Quantum Yield Measurements of the $\text{NO}-\text{O}$ Reaction and its use as a Standard for Chemiluminescent Reactions, *J. Chem. Phys.*, **4** 0, pp. 64-70, 1964.
- Holtzclaw, K.W., Fraser, M.E., and Gelb, A., Infrared Emission from the Reaction of High Velocity Atomic Oxygen with Graphite and Polyethylene, in press, *J. Geophys. Res.*, 1990.
- Kenner, R.D., Ogryzlo, E.A., Orange chemiluminescence from NO_2 , *J. Chem. Phys.* **8** 0, 1-6, 1984.
- Kofsky, I.L. and Barrett, J.L., Spacecraft Glows from Surface-Catalyzed Reactions, *Planet. Space Sci.* **3** 4, 665, 1986.
- Mende, S.B., Garriott, D.K., and Banks, P.M., Observations of Optical Emissions on STS-4, *Geophys. Res. Lett.* **1** 0, 122, 1983a.
- Mende, S.B., Vehicle Glow, AIAA-83-2607-CP, presented at Shuttle Environment and Operations Meeting, Washington, DC, 1983b.
- Mende, S.B., Nobles, R., Banks, P.M., Garriott, D.K., and Hoffman, J., Measurement of Vehicle Glow and Space Shuttle, *J. Spacecraft Rockets* **2** 1, 374, 1984a.
- Mende S.B., Banks, P.M., and Klingelsmith, III, D.A., Observation of Orbiting Vehicle Induced Luminosities on the STS-8 Mission, *Geophys. Res. Lett.* **1** 1, 527, 1984b.
- Mende, S.B. and Swenson, G.R., Vehicle Glow Measurements on the Space Shuttle, AIAA-85-0909, presented at AIAA 20th Thermophysics Conference, Virginia, 1985.
- Mende, S.B., Swenson, G.R., Clifton, K.S., Gause, R., Leger, L., and Garriott, O.K., Space Vehicle Glow Measurements on STS41D, *J. Spacecraft* **2** 3, 189, 1986.
- Mende, S.B., Swenson, G.R., and Llewellyn, E.J., *Adv. Space Res.* **8** (1), 229, 1988.
- Orient, O. J., Chutjian A, Murad E., Recombination reactions of 5 eV $\text{O}(^3\text{P})$ atoms on a MgF_2 surface. *Phys. Rev. A, Rapid Comm.* **4** 1, 4106-4108 (1990).
- Paulsen, D.E., Sheridan, W.F., Huffman, R.E., Thermal and recombination emission of NO_2 *J. Chem. Phys.* **5** 3, 647-658 (1970).
- Sackett, P.B., Yardley, J.T. *Chem. Phys. Lett.* **9** 61d2 (1971).
- Slanger, T.G., Deductions from Space Shuttle Glow Photographs, *Geophys. Res. Lett.* **1** 3, 431, 1986.
- Swenson, G.R., Mende, S.B., and Clifton, K.S., Ram Vehicle Glow Spectrum: Implication of NO_2 Recombination Continuum, *Geophys. Res. Lett.* **1** 2, 97, 1985.
- Swenson, G.R., Mende, S.B., and Llewellyn, E.J., The Effect of Temperature on Shuttle Glow, *Nature* **3** 2 3, 519, 1986.

Figure 1

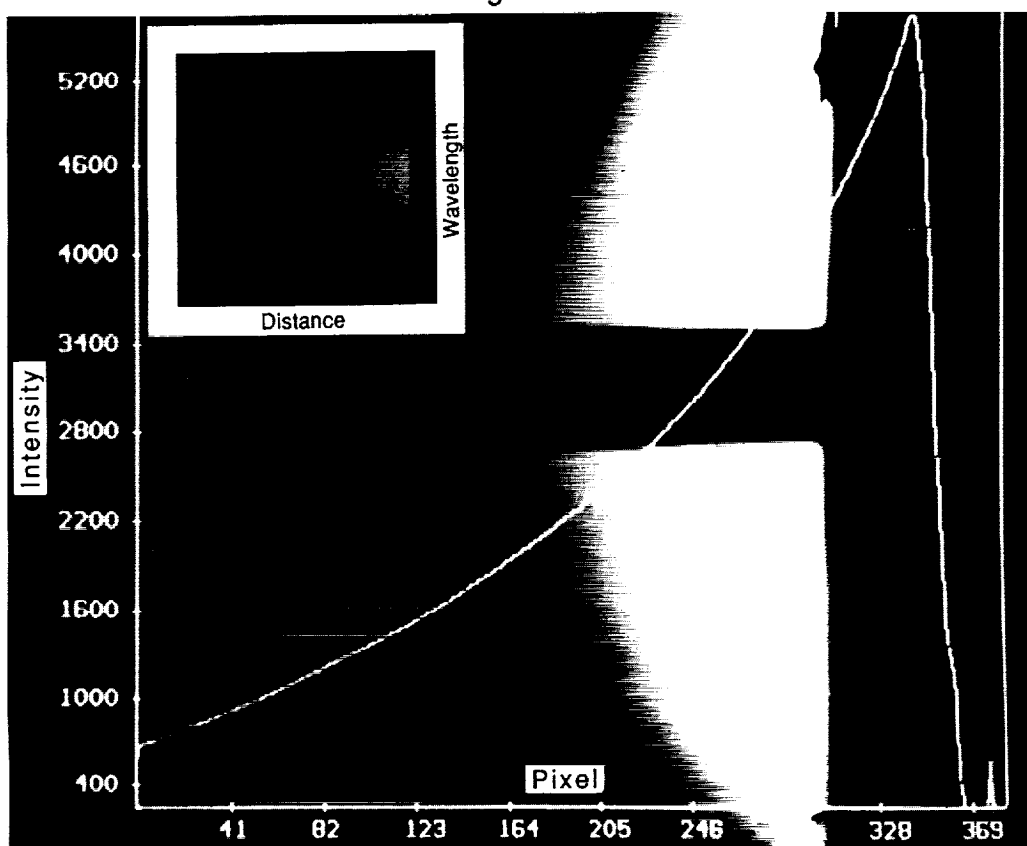


Figure 2

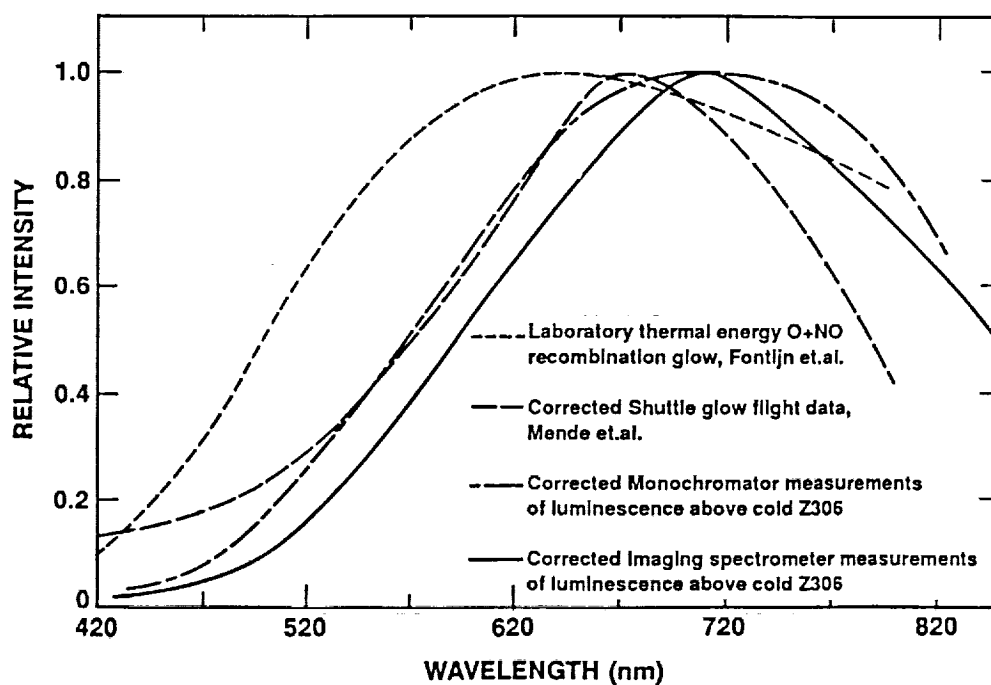


Figure 3

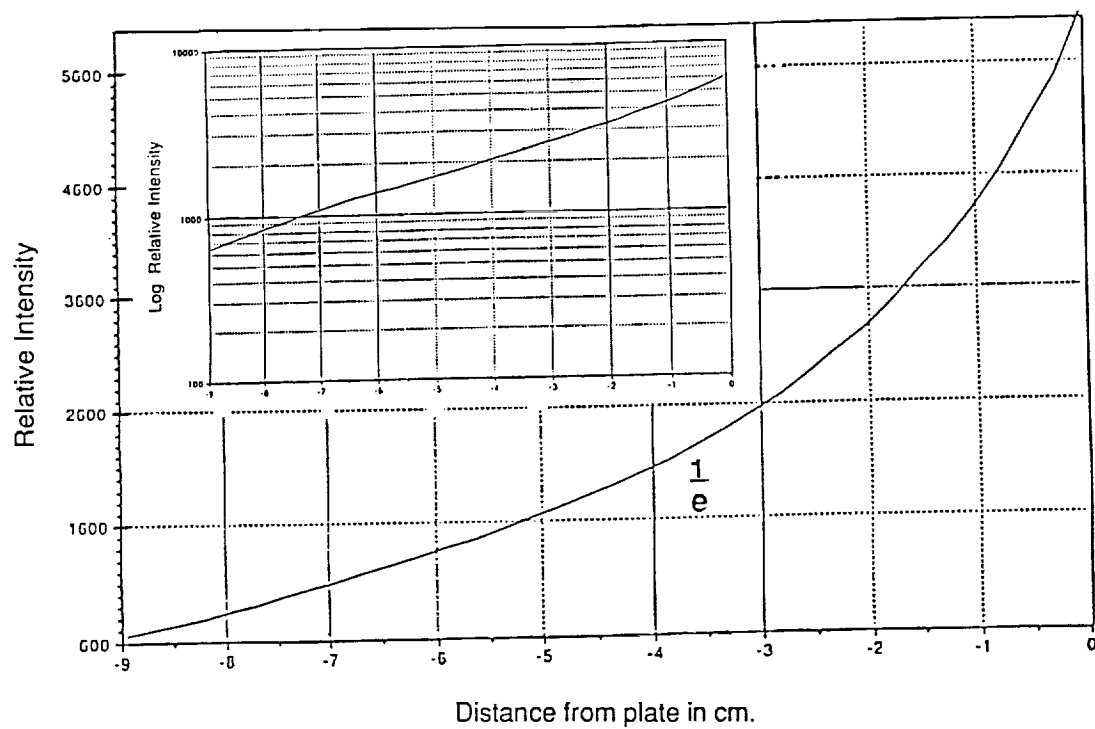


Figure 4

